Thin Films Division
Room A124-125 - Session TF-MoM
Thin Films for Electrochemistry and Energy Storage

Moderators: Parag Banerjee, University of Central Florida, Jason Avila, U.S. Naval Research Laboratory

8:20am **TF-MoM-1 Enabling Energy Dense Lithium Batteries Using Thin Film Technology**, ***Wyatt Tenhaeff***, University of Rochester **INVITED**

As new materials and electrochemical cell compositions are developed to meet the ever-increasing demand for high capacity, long-life lithium batteries, thin film deposition technology provides critical capabilities for engineering key interfaces within these batteries. This presentation will present our efforts to address challenges in lithium metal and silicon anodes. Thin films are integrated as ultrathin solid electrolytes in Li metal batteries and as protective coatings on Si anodes to limit undesirable side reactions.

Key requirements for electrolytes in solid-state lithium metal batteries are a large electrochemical stability window and low area-specific resistance (ASR). Solid electrolytes must also possess robust mechanical properties to accommodate large-scale production and integration into conventional lithium battery cell designs. To realize these properties, 50 nm-thick films of lithium phosphate oxynitride (Lipon) were deposited onto microporous polymer separators (Celgard) using RF magnetron sputtering. These separators provide a low ASR due to the thin, dense Lipon film; the total resistance of the separator was determined to be 40 Ω cm^2 in alkyl carbonate electrolytes, which is much lower than traditional ceramic electrolytes membranes, such as those fabricated from Garnet and NASICON-class of solid electrolytes. Furthermore, these composite separators inhibit chemical cross-diffusion and reaction between anode and cathode in both Li-S and Li-$LiMn_2O_4$ cells.

Silicon is also an intriguing next-generation anode offering charge capacities comparable to lithium metal, yet significant challenges arise from the >300% volume expansion of Si during lithiation. To address continual electrochemical reduction of lithium ion battery electrolyte on Si anodes, nanoscale, conformal polymer films were synthesized as artificial solid electrolyte interface (SEI) layers. Initiated chemical vapor deposition (iCVD) was employed to deposit poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) (pV4D4) onto silicon thin film electrodes. 25 nm-thick pV4D4 films on Si electrodes improved initial coulombic efficiency by 12.9% and capacity retention over 100 cycles by 64.9% relative to untreated electrodes. PV4D4 coatings also improved rate capabilities, enabling higher lithiation capacity at all current densities. Post-cycling FTIR and XPS showed that pV4D4 inhibited electrolyte reduction and altered the SEI composition, with LiF formation being favored. This work will guide further development of polymeric artificial SEIs to mitigate electrolyte reduction and enhance capacity retention in Si electrodes.

9:00am **TF-MoM-3 Molecular Layer Deposition of Organic Li-containing Thin Film for Li Ion Solid-state Batteries**, ***Haotian Wang***, University of Maryland, College Park

High performance 3D solid-state Li ion batteries require uniform and conformal coating of solid electrolytes with high mechanical compliance, to enable the usage of high energy density anodes, such as Si, and maintain a good electrode-electrolyte contact during cycling. Molecular layer deposition (MLD) is a vapor phase deposition technique that deposits thin films in a layer by layer manner. The incorporation of organic moieties into the resulting MLD thin films potentially provides enhanced mechanical flexibility while retaining the high uniformity and conformality, making this technique promising for applications in the next generation 3D solid state batteries.

In this work, we are presenting a fundamental study of organic Li-containing thin film by MLD. A comprehensive understanding of the organic-inorganic reaction and growth mechanism was obtained based on a model chemistry with Li tertbutoxide (LiO^tBu) and propanediol (PPD). The ALD-like growth temperature window, linear growth and the self-limiting behavior were observed by employing in-situ ellipsometry during deposition. Chemical structure of the film grown by LiO^tBu and PPD was characterized by X-ray photoelectron spectroscopy (XPS) and simulated by ab-initio calculation. Based on both the experimental characterization and theoretical calculation, a hybrid inorganic-organic Li-containing material, Li propane oxide, with well-defined stoichiometry ($Li_{1.6}C_3H_6O_{2.2}$) was successfully synthesized via MLD. Additionally, nucleation delay during film growth was observed, indicating an island growth and crystal formation. Single crystal nucleus with cubic crystal structure at early growth stage was observed by transmission electron microscopy (TEM), while at later growth stage, nucleus coalesced and formed polycrystalline thin film with high surface roughness. To reduce the surface roughness and enhance the applicability of the MLD film in high aspect ratio geometries, we applied nitrogen plasma to the Li propane oxide MLD process. The nitrogen plasma modified MLD process showed no nucleation delay and was later used as seeding for Li propane oxide growth. A significant attenuation of surface roughness of Li propane oxide MLD films grown on this seeding layer was observed. The understanding of the inorganic-organic reaction and the development of the seeding layers for the Li-containing thin film will benefit directly to the flexible and three-dimensional solid state battery research.

9:20am **TF-MoM-4 Organic/Inorganic Solid Electrolytes and Electrode Coatings for 3D Lithium-ion Microbatteries**, ***Ryan Sheil***[1], *J Lau,* University of California, Los Angeles*; K Jungjohann,* Sandia National Laboratories*; J Yoo,* Los Alamos National Laboratory*; B Dunn, J Chang,* University of California, Los Angeles

Lithium-ion batteries have been an enabling factor in the success of consumer electronics and have the potential to offer energy storage solutions for microelectromechanical systems (MEMS), such as sensors for IoT and biomedical applications. Three-dimensional battery architectures allow for an effective decoupling of the areal energy and power density resulting in improved areal footprint utilization required of these small devices. In 3D battery designs, the short distances between the anode and cathode improve the transport properties allowing for high areal power densities and the high aspect-ratio nature of the electrodes promotes high areal energy densities. One requirement in the utilization of 3D based electrodes is the incorporation of a solid electrolyte that can be coated pinhole free and conformally on high aspect ratio structures. The solid electrolyte material must be ionically conductive, electronically insulating, and be flexible to withstand the volume expansion and contraction of the electrode during charge and discharge.

The self-limiting nature of atomic layer deposition allows for precise thickness control across high aspect ratio structures. ALD $Li_xAl_ySi_zO$ was synthesized utilizing lithium tert-butoxide (LTB), trimethyl aluminum (TMA), and tris(tert-butoxy) silanol (TTBS). ALD $Li_xAl_ySi_zO$ was integrated with high aspect ratio SiGe nanowires for in-situ TEM characterization, where the chemical, structural, and morphological changes of the electrode/electrolyte system were characterized in-situ during lithiation and delithiation. An ALD $Li_xAl_ySi_zO$-coated $Si_{0.4}Ge_{0.6}$ nanowire demonstrates lithiation and delithiation with an intact solid state electrolyte layer with ~39% radial expansion observed upon lithiation. To further improve the mechanical properties for integration on high capacity/large volume expansion anodes, an MLD process was explored to synthesize lithium alkoxide and aluminum alkoxide utilizing trimethyl aluminum and lithium tert-butoxide coupled with glycerol. Incorporation of the MLD, ALD, and MLD/ALD coatings were integrated with Si and Co_3O_4 elecrodes, where improvements to cycling stability and coulombic efficiency were observed. $Li_xAl_ySi_zO$ coated Co_3O_4 thin films exhibited improved coulombic efficiency (99.5% (coated), 90.5% (uncoated) and capacity retention (2458 mAh/cm^3 (coated), 2038 mAh/cm^3 (uncoated)) after 100 cycles at 2C.

9:40am **TF-MoM-5 Structural Rearrangement in $Li_xV_2O_5$ Thin Films, a Cathode Material for All-solid-state Batteries**, ***Angelique Jarry***, University of Maryland, College Park*; N Pronin, M Walker,* The Ohio State University*; J Ballard,* University of Maryland*; D Stewart,* University of Maryland, College Park*; L Brillson,* The Ohio State University*; G Rubloff,* University of Maryland, College Park

The requirements to enable all-solid-state batteries (SSBs) are extremely stringent and necessitate control of the chemistry and interfaces over a wide structural length and long-time scales. Investigations using multi-probe approaches have confirmed that surface composition, defects, structure, and morphology of the electrodes/electrolyte themselves has a strong impact on interfacial processes. Therefore, to understand how to overcome the barriers related to the implementation of SSBs, it is necessary to start with pure, well-defined models systems such as cathode thin films. V_2O_5 is of particular interest due to the large interlayer spacing of its metastable varieties that allows a topochemical de-intercalation of various cation ($M_xV_2O_5$ withM = Li, Na, Mg). However this cation de-insertion leads to structural distortion/surface reconstruction that impedes

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[1] **TFD James Harper Award Finalist**

the cathode performance. A detailed understanding of these degradation mechanisms is needed to identify the appropriate remedies.

In this work, V_2O_5 thin films of ~500 nm were produced by atomic layer deposition (ALD) on sputtered gold on silicon substrate. The films were subsequently electrochemically lithiated in liquid electrolytes by galvanostatic cycling i.e, $Li_xV_2O_5$ with x < 2. We investigated the effects of lithiation on the structural characteristics and surface morphology of $Li_xV_2O_5$ thin films as a function of depth through multiple methods. Change in the crystallinity and local atomic structure were probed with Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), optical/scanning electron microscopy and, atomic force microscopy (AFM). We demonstrated that partial lithiation of V_2O_5 results in reduction of the vanadium that is accompanied by a progressive surface hydroxylation and amorphization of the films. At high lithium content, significant non reversible structural rearrangements associated with the destabilization of the V-O framework are observed. The correlation between the lithium content, structural stability, electrode's surface activity and electrochemical performance will be presented and discussed.

Acknowledgement

This work was supported by the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science and by the NSF grant DMR-18-00130.

10:00am **TF-MoM-6 Atomic Layer Deposition and Performance of Sodium and Potassium Electrolytes for Conformal Solid State Batteries**, ***Blake Nuwayhid**, A Jarry, G Rubloff, K Gregorczyk,* University of Maryland, College Park

Solid-state batteries (SSBs) provide significant advantages over conventional liquid electrolyte based batteries, such as their non-flammable nature and improved chemical stability. Specifically, thin film SSBs possess the ability to provide high power densities due to a shorter transport pathway and are compatible with semiconductor device manufacturing. The fabrication of 3D thin film SSBs through conformal deposition processes is extremely promising due to the dramatic enhancement in both energy and power densities compared to planar cells. Our group recently demonstrated the fabrication of the first fully conformal 3D Li-based thin film SSBs, in which all battery components were deposited by Atomic Layer Deposition (ALD).[1] This was made possible through the development of a new lithium phosphazene (Li_2PO_2N) solid electrolyte. Sodium and potassium ion batteries are interesting as well for SSB applications due to the lower cost and higher abundance of the alkali metals compared to lithium. However, few such efforts have been put into solid state systems, and none in 3D thin film SSBs. In this presentation, we will discuss the development of conformal sodium phosphorous oxynitride (NaPON) and potassium phosphate (KPO) ion-conductors, and their potential in 3D thin film SSBs. Similar to our previously published LiPON ALD process[2], NaPON and KPO processes use the thermal reaction of sodium tert-butoxide or potassium tert-butoxide, with diethyl phosphoramidate. The growth behavior of NaPON and KPO were very similar, exhibiting a linearly increasing growth rate of 0.1-1.0 Å/cycle at 250-400 °C, but no temperature window was observed. An ultra-high vacuum chamber coupled the ALD reactor to a X-ray Photoelectron Spectrometer, allowing for sensitive film characterization as a function of temperature. Characterization was also complemented by Raman and IR spectroscopy to reveal differences in the phosphorus oxynitride bonding networks. The structure of NaPON resembled that of LiPON, containing similar atomic ratios (P/N = 1) and 2 nitrogen species (=N– and >N–), whereas KPO films contained only 1% nitrogen and a considerable amount of carbon incorporation. We will also highlight the electrochemical behavior of the films in planar solid-state cells and 3D systems in high aspect ratio substrates.

1. Pearse, A.; Schmitt, T.; Sahadeo, E.; Stewart, D. M.; Kozen, A.; Gerasopoulos, K.; Talin, A. A.; Lee, S. B.; Rubloff, G. W.; Gregorczyk, K. E. *ACS Nano* **2018,***12*, 4286-4294.

2. Pearse, A.; Schmitt, T. E.; Fuller, E. J.; El-Gabaly, F.; Lin, C. F.; Gerasopoulos, K.; Kozen, A. C.; Talin, A. A.; Rubloff, G.; Gregorczyk, K. E. *Chemistry of Materials* **2017,***29*, 3740-3753.

10:40am **TF-MoM-8 ALD as Tool for Bottom-up Synthesis of Catalyst Powders**, ***Frank Rosowski**,* BASF Se, Germany **INVITED**

Atomic Layer Deposition is mainly applied in microelectronics as a thin film deposition technique. In academic research, ALD is also applied for synthesis of battery materials and catalysts. The main challenge for ALD in these research fields is the morphology of the substrate materials, usually small particles with high specific surface areas, e.g. up to 1000 m^2/g for zeolites. Catalytic reactors can hold packed beds of several cubic meters of catalyst. The high specific surface areas and the amounts in which such catalysts are needed require safe and efficient ways of dosing ALD precursors without bypass and waste. And while mass and heat transport limitations play only a minor role in the case of flat substrates, these phenomena need to be considered when coating large amounts of powder.

At BasCat, ALD is used in several projects to synthesize and modify catalysts. Some research is done along well-established lines of work in the field of supported metal catalysts, e.g. modifying supported metal catalysts with metal oxide layers, but the focus lies on catalysts used for selective oxidation reactions, typically consisting of mixed metal oxides or phosphates. Catalysts are usually prepared in two batch sizes. For establishing suitable ALD process conditions, a sample size of about 1 cm^3 is used. In a second step, catalyst amounts of 10–25 cm^3 are prepared. It is important that process conditions established on the small scale are easily transferrable to the large scale.

For this purpose, a new and unique test facility was installed at BasCat equipped with a thermogravimetric balance as analytical small scale ALD reactor and a second reactor for catalyst synthesis on a large scale via ALD.[1] Based on our first ALD results, a fixed bed was chosen as reactor geometry for the analytical reactor and the synthesis reactor.

In order to check the feasibility of our new in situ method and the ALD performance of our fixed bed reactor, first studies covered the deposition of alumina on a typical catalyst support, a silica with high surface area (Davisil 636). It was shown that the fixed bed geometry is suitable for ALD, that the substrate is homogeneously covered, and that scaling-up from 1 cm^3 to 10 cm^3 is possible.[2]

The combination of analytical reactor and synthesis reactor was then successfully used for modifying supported metal catalysts with layers of alumina, alucone, and zinc oxide. Other works included the deposition of rhenium on silver and phosphorus on vanadia.[3]

[1] Strempel et al., *Rev. Sci. Instrum.*, 074102. 2017

[2] Strempel et al., F.,*Nanomaterials*, 365. 2018

[3] Strempelet al., *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, 01A135. 2016

11:20am **TF-MoM-10 Strategies for the Stabilization of Metal Anodes for Li and Na Metal Batteries**, ***Yang Zhao**[1], X Sun,* University of Western Ontario, Canada

Li-metal batteries (LMBs) and Na-metal batteries (NMBs) are considered as the promising candidates to replace the conventional Li-ion batteries due to their high theoretical energy density. Li metal and Na metal are the ultimate choices as anodes to achieve their high energy density due to the high specific capacity, low electrochemical potential and lightweight [1]. However, as alkali metals, both Li and Na metal anodes suffer from serious challenges including 1) dendrite formations and short circuits; 2) Low Coulombic efficiency (CE) and poor cycling performance; and 3) Infinite volume changes. This presentation mainly focuses on the design of multiple strategies for the stabilization of Li and Na metal anode for LMBs and NMBs.

Solid electrolyte interphase (SEI) layer is one of the key factors for the Li and Na deposition behaviors [2]. We developed different approaches to fabricate the artificial SEI with significantly improved electrochemical performances. Firstly, we have demonstrated different ultra-thin protective layers for Li and Na metal anodes by atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques, including Al_2O_3, alucone, and polyurea, et al [3]. More recently, we designed a dual-protective layer for Li metal anode with precisely controlled thicknesses, compositions and mechanical properties [4]. Secondly, we developed the in-situ solution-based methods to fabricate the Li_3PS_4 and Na_3PS_4 as protective layers for both Li and Na metal anodes with enhanced performances and reduced dendrite growth [5].

To address another challenge of volume change, 3D conductive interlayers and hosts have been designed for Li and Na metal anodes. Carbon paper (CP) and modified CP with carbon nanotubes have been used as host/interlayer with excellent electrochemical performance under high current density and high capacity [6].

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[1] **Late-Abstract Energy Transition Symposium Theme Award**

In conclusion, we developed the different approaches, including protective layers fabricated by ALD/MLD and solution methods, interlayers, and 3D skeleton design, for Li and Na metal anodes with enhanced electrochemical performances and reduced dendrite growth. Meanwhile, the ideas have been also applied to solve the practical issues for testing Li and Na metal batteries.

[1] ***Energy & Environmental Science***, 2018, 11, 2673

[2] ***Joule***, 2018, 2, 2583

[3] ***ACS Energy Letters***, 2018, 3, 899; ***Small Methods***, 2018, 2, 1700417; ***Advanced Materials***, 2017, 29, 1606663; ***Nano Letters***, 2017, 17, 5653; ***Advanced Materials***, 2019, 31, 201806541

[4] ***Matter***, 2019, in press

[5] ***Journal of Materials Chemistry A***, 2019, 7, 4119

[6] ***Nano Energy***, 2018, 43, 368; ***Energy Storage Materials***, 2018, 15, 415; ***Small***, 2018, 14, 1703717

11:40am **TF-MoM-11 Competition Between Incorporation and Desorption of Nitrogen in Plasma-Enhanced Atomic Layer Deposition of Cobalt and Cobalt Nitride Catalysts***, **Gerben van Straaten**,* Eindhoven University of Technology, The Netherlands, Netherlands*; H Fredriksson,* Syngaschem BV, Netherlands*; R Deckers,* Eindhoven University of Technology, Netherlands*; M Vos,* Eindhoven University of Technology, The Netherlands, Netherlands*; K Weststrate,* Syngaschem BV, Netherlands*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; A Creatore,* Eindhoven University of Technology, Netherlands

Cobalt catalysts have various applications in the chemical industry. Most prominently, metallic Co is used in the production of synthetic fuels via the Fischer-Tropsch process, while cobalt nitrides (with the general formula CoN_x) are being explored as noble-metal free electro-catalysts for the oxygen evolution reaction. Atomic Layer Deposition (ALD) of Co and CoN_x thin films and nanoparticles can be achieved using a variety of Co precursors with NH_{3-} plasma[1]. Moreover, the precursors $Co(CO)_8$ and $CoCp_2$ can yield either metallic Co or CoN_x, depending on temperature[2]. We will demonstrate here that this is due to the metastable nature of CoN_x.

We have found that film deposition below 350°C onto thermally grown SiO_2 using $CoCp_2$ and an inductively coupled NH_3 plasma yielded Co_2N, while deposition at higher temperatures resulted in Co with traces of N. To gain insight into the incorporation of N into the films, Spectroscopic Ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS) were performed on 20 nm Co films exposed to NH_3 plasma. These measurements revealed that at 150°C, 30 min of plasma exposure resulted into the formation of a 5 nm thick N-enriched diffusion layer at the film surface. However, the nitridation process is temperature-dependent: at 350°C and above, no N incorporation into the bulk of the layer was observed. The origin of this temperature dependence was analyzed using Temperature-Programmed Desorption (TPD), which showed that N could be released from the low temperature plasma-treated layers in two stages. Around 270°C, N desorbed from the surface, but no loss of N from the bulk of the Co layer was observed. Subsequently, starting at 350°C, complete effusion of bulk N took place, allowing the film to relax back to its original thickness.

These results show that at low temperatures N is incorporated into the growing film from the NH_3 plasma, leading to the formation of homogeneous CoN_x films, but at elevated temperatures, N desorption outpaces incorporation and metallic Co is formed instead. Thus, it is possible to deposit Co and CoN_x catalysts with controlled stoichiometry by balancing N incorporation and desorption. Preliminary measurements show that Co nanoparticles and thin films deposited in this way are capable of catalyzing the methanation reaction; further characterization of their activity is currently ongoing.

[1] M. F. J. Vos, G. van Straaten, W. M. M. Kessels, and A. J. M. Mackus, *J. Phys. Chem. C*, p. acs.jpcc.8b06342, Sep. 2018.

[2] H.-B.-R. Lee and H. Kim, *Electrochem. Solid-State Lett.*, vol. 9, no. 11, p. G323, Nov. 2006.

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